

Construction and operation of a novel mediator- and membrane-less microbial fuel cell

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Abstract

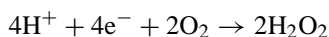
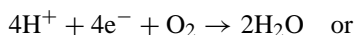
A membrane-less microbial fuel cell (ML-MFC) with the internal resistance of 3.9 MΩ was used to enrich a microbial consortium oxidizing electron donors with concomitant current generation. Within 4 weeks the system generated a stable current of 2 mA. The current yield was less than 10%. Forced aeration to the cathode compartment generated higher current, but the yield was similar. Use of a cathode with a higher affinity for oxygen could improve the current yield. Additions of NaCl or HCl increased the current generation further with the current yield of 15%. Aerobic microbes turned out to be the predominant oxygen consumer at the cathode. Based on these findings suggestions are made for a ML-MFC configuration with better performance.

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1. Introduction

A microbial fuel cell (MFC) is a device that converts chemical energy to electrical energy with the aid of the catalytic reaction of microorganisms [1,2]. An MFC consists of anode and cathode separated by a cation-specific membrane. In the anode compartment of an MFC microorganisms oxidize fuel (substrate) generating electrons and protons. The protons and electrons are transferred to the cathode compartment, the protons through the membrane and the electrons through the external circuit. They are consumed reducing oxidant at the cathode, usually oxygen supplied by aeration;



In a typical MFC, an anodic electrode potential is developed when the electrons from the oxidation of fuel by mi-

croorganisms are available to the electrode. Electrons cannot be transferred from the normal microbial electron transport systems to the electrode due to the non-conductive nature of the cell surface structures. Electrochemical mediators were employed to render electron transfer from the microbial cells to the electrode. The mediators are usually toxic phenolic compounds. Therefore, the long-term operation of mediated MFCs cannot be achieved with limited commercial applications although MFCs can be used for various purposes including biosensors [3,8,11,12] and electricity generation [1,9].

Previous studies showed that an MFC could be operated without mediators using an electrochemically active metal-reducing bacterium, *Shewanella putrefaciens* [3–5]. The bacterial cells in the anode of MFC consumed substrate as fuel and transferred electrons directly to the electrode. In the subsequent studies it has been shown that electrochemically active microbes can be enriched using a fuel cell type electrochemical cell [2]. Several steps have been identified as the limiting steps in a mediator-less MFC [6]. They are (1) fuel oxidation at the anode, (2) electron transfer from microbial cells to anode, (3) resistance of the circuit, (4) proton

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transfer through the membrane, and (5) oxygen reduction at the cathode.

In a mediator-less MFC, as in other MFCs, the membrane separates the anode from the cathode and the membrane functions as an electrolyte that plays the role of an electronic insulator and allows protons to move through. These functions of the membrane are believed to be indispensable in the operation of an MFC.

Application of MFCs for wastewater treatment is very attractive due to energy recovery from waste as well as reducing production of excess sludge, disposal of which is very expensive. It is expected that this process would generate much less excess sludge than a conventional activated sludge process, since the major part of energy available from the oxidation of the organic contaminants is converted to electricity, and the remaining energy is used for microbial growth. However, the use of membranes can limit the application of an MFC to wastewater treatment. As mentioned above proton transfer through the membrane can be a limiting factor especially with fouling expected due to the suspended solid and soluble contaminants in a large-scale wastewater treatment process. Also membranes are expensive.

A fuel cell consisting of an anode embedded in marine sediment and a cathode in overlying seawater was used successfully to generate electricity [14,15]. The anode embedded in the sediment was enriched with bacteria belonging to the family *Geobacteraceae* [16].

In this study attempts were made to develop a mediator-less MFC without using a membrane. Membranes are the major cost for the construction of an MFC. A membrane-less MFC could improve the economic feasibility of the process to treat wastewater by reducing not only the capital investment but also the operation cost for the membrane maintenance. In this study a fuel cell was used to treat wastewater in a continuous mode. To the authors' knowledge up to now, MFCs have not been used for wastewater treatment.

2. Materials and methods

2.1. Membrane-less microbial fuel cell and its operation

Fig. 1 shows the schematic diagram of the membrane-less microbial fuel cell (ML-MFC) used in this study. It was made of polyacrylic plastic. The anode was at the bottom, and the cathode at the top of cylinder-shaped reactor with a diameter of 10 cm. Glass wool and glass bead of 10 cm in depth was placed on the upper of the anode. Graphite felt (196.0 g, GF series, GEE Graphite Limited, Dewsbury, West Yorkshire, UK) as roll form was used as the anode, and the cathode of the same material (53.3 g) in a disk form. The total height of the reactor was 100 cm, and the distance between the anode and cathode was 10 cm including glass wool and glass bead. In some experiments the distance was increased to 30 cm. The apparent surface areas of anode and cathode were 465 and 89 cm², respectively. In some experiments the graphite

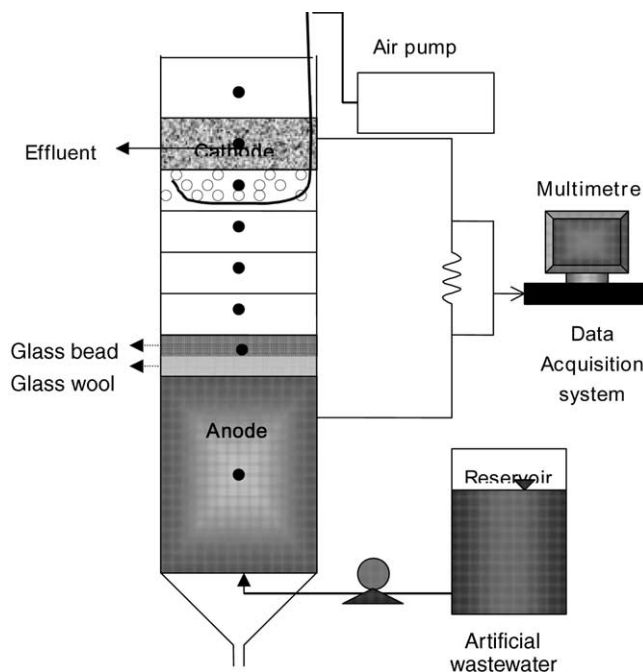


Fig. 1. Schematic diagram of ML-MFC. ●: Sampling port. The anode was at the bottom, and the cathode at the top of reactor with the diameter of 10 cm made of polyacrylic plastic. Glass wool and glass bead of 10 cm in depth was placed on the upper of the anode. Graphite felt (196.0 g, GF series, GEE Graphite Limited) as roll form was used as the anode, and the cathode of the same material (53.3 g) in a disk form. The total height of the reactor was 100 cm with varying distance between the anode and cathode.

cathode was replaced with platinum-coated graphite, which was prepared as previously described [13].

The fuel was supplied to the bottom of the anode and the effluent left through the cathode compartment at the top. The electrodes were connected with platinum wire through a resistance of 10 Ω and a multimeter. The internal resistance was 3.9 M Ω . The fuel was supplied at the rate of 0.28 ml/min at the initial stage and the feeding rate of fuel increased up to 1.83 ml/min. The cathode compartment was aerated at various rates for the cathode reaction. In some experiments NaCl or HCl were added to the bottom of cathode.

2.2. Wastewater

A modified artificial wastewater (AW) containing glucose and glutamate was used as model wastewater throughout the study [7]. Filter-sterilized glucose and glutamate solution (10 ml) was mixed with salt solution. The salt solution was prepared by mixing 10 ml trace mineral solution [17], 50 ml phosphate buffer (1 M, pH 7.0), and 930 ml distilled water. The trace mineral salt solution contained (NH₄)₂SO₄, 0.56 g; MgSO₄·7H₂O, 0.20 g; CaCl₂, 15 mg; FeCl₃·6H₂O, 1 mg; MnSO₄·H₂O, 20 mg; NaHCO₃, 0.42 g. The salt solution was autoclaved at 121 °C for 15 min and cooled under oxygen-free nitrogen gas before being mixed with filter sterilized glucose and glutamate solutions. The BOD of AW

was 300 mg/l. The AW was made and maintained under a nitrogen atmosphere by connecting to a nitrogen containing gas-tight bag with a volume of 5 l (Alltech, Deerfield, IL, USA).

2.3. Enrichment of electrochemically active microbes for operating MFC

The membrane-less MFC was inoculated with activated sludge (50 ml) collected from Jungryang Sewage Treatment Plant (Seoul, Korea) and fed with AW (BOD of 300 mg/l) at a continuous mode with flow rate of 0.28 ml/min. A stable current was generated from the reactor after about 4 weeks of continuous feeding at this condition.

2.4. Analyses

The potential was measured using a multimeter (Keithley Instruments, Inc., Cleveland, OH, USA) and recorded every 5 min to a personal computer through a data acquisition system (Testpoint, Capital Equipment Co., Richmond, VA, USA). The COD_{Cr} was determined by standard methods using chromate as the oxidant [10]. The dissolved oxygen concentration (DO) was measured using a DO meter (Orion Model 850, Beverly, MA, USA) and the pH was measured using a pH meter (pH/ION Meter DP-880, Dong-Woo Medical System, Seoul, Korea). The current yield was calculated as (observed current/theoretical current) \times 100 (%), where theoretical current was calculated based on the COD consumption rate. The COD consumption rate was multiplied by 12 A/mg COD to calculate the theoretical current. The figure, 12 A/mg COD is current expected from the consumption rate of 1 mg COD/s, $1/32 \times 4 = 0.125$ mmol electron/mg COD per s where 32 is the molecular weight of O_2 , which is multiplied by Faraday constant (0.125 mmol electron/mg COD per s $\times 96.487$ A s/mol electron $\equiv 12$ A/mg COD).

All experiments were repeated more than three times after the enrichment, and the mean values or the typical results are presented.

3. Result and discussion

3.1. Enrichment

An ML-MFC was used to enrich electrochemically active microbes using activated sludge as inoculum and AW as fuel at a feeding rate of 0.28 ml/min (Fig. 2). The cathode compartment was aerated at a rate of 40 ml/min. The current slowly increased for 2 weeks, and a rapid increase was observed in the next 2 weeks to the maximum current of over 2 mA. The current was maintained stably for over a year under the given conditions, and the open circuit potential was about 0.8 V. The COD of the effluent decreased gradually from 300 mg/l to less than 30 mg/l during the enrichment.

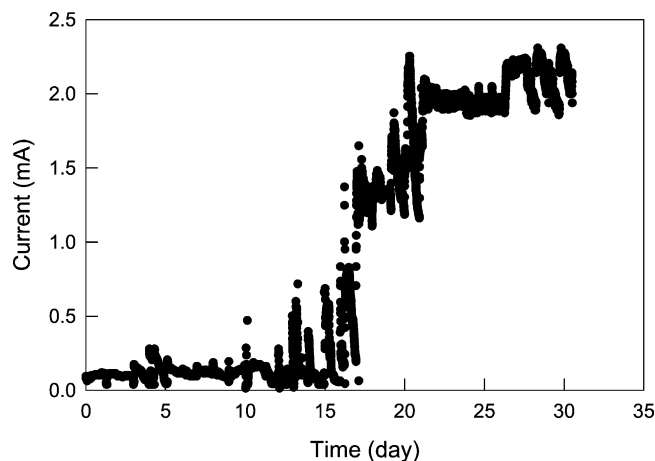


Fig. 2. Start-up of a ML-MFC. The reactor was inoculated with anaerobic activated sludge and fed with the AW continuously at the HRT of 20 days.

During the enrichment process the fuel was fed at the rate of 0.28 ml/min with an hydraulic retention time (HRT) of 6.7 days. After the enrichment process the reactor was run at HRT of 1 day (feeding rate of 1.83 ml/min) with a similar COD removal efficiency. The COD removal efficiency was 526.67 g/m³ day with the efficiency over 90%. These results show that the ML-MFC can be used as a wastewater treatment process.

3.2. Effect of external resistance

The ML-MFC was fed with AW at a feeding rate of 0.28 ml/min and the current was recorded with different resistances across the anode and cathode to establish the relationship between resistance and current as well as between resistance and COD removal. As expected, the higher the resistance the lower the current generated, and more COD was removed at lower external resistance (Fig. 3). The current of 2.0 mA was obtained at the 10 Ω of resistance either after resistance up-shift or down-shift. These results show that the reactor behaves as a typical fuel cell.

At low resistance the electrons move more easily through the circuit than at high resistance, oxidizing electron carriers of the microbes in the anode. Higher fuel oxidation by the microbes is expected with high ratio of oxidized electron carriers of the culture at a low resistance. The reactor can be operated at a low resistance to remove organic contaminants at a high rate.

3.3. Distance between the electrodes

The ML-MFC was operated with the distance between the anode and cathode of 30 cm at different external resistances, and the performance was compared with that recorded from the normal run with the distance of 10 cm. AW was fed at the feeding rate of 1.83 ml/min. The current density was calculated and plotted against potential and power density at different resistance to obtain the polarization curve (Fig. 4).

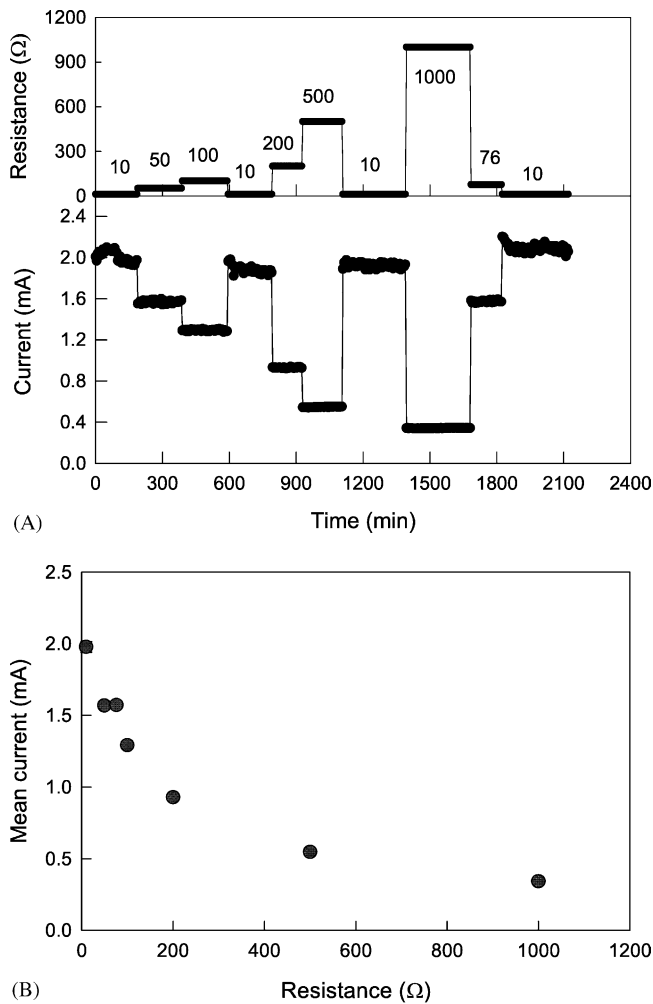


Fig. 3. Current generation through the different external resistance. (A) Current monitoring with various resistance; (B) relationship between resistance and current.

Higher potential was maintained from the runs with the distance of 10 cm than those of 30 cm in all current densities tested. The highest power density of 1.3 mW/m^2 was achieved at the current density of $6\text{--}9 \text{ mA/m}^2$, which was obtained with the resistance of 200 and 100 Ω , respectively. This power density value was lower than 320 mW/m^2 , which was obtained from MFCs with membrane (unpublished data). These results show that the electrode surface in this bigger reactor is used less efficiently than those of smaller reactors used as BOD sensors [7]. The power density was higher from the runs with the distance of 30 cm than the other when the current density was over 6 mA/m^2 , but slightly lower when the current density was lower than that value.

These results suggest that the mass transfer between two electrodes is a limiting factor, probably proton transfer from the anode to the cathode. In this sense a ML-MFC should be constructed to place the electrodes as close as possible keeping the internal resistance high enough to avoid an electrical leak.

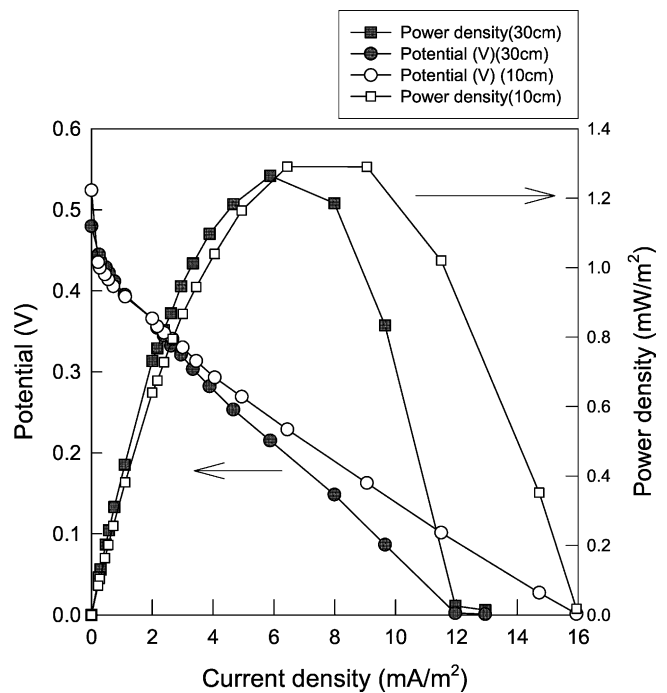


Fig. 4. Polarization curve of the ML-MFC operated with the distance between the anode and cathode of 10 cm (open symbols) and 30 cm (closed symbols). The reactor was run at various resistances. At each resistance the current density was calculated and plotted against potential (circle) and power density (square).

3.4. Effects of aeration into the cathode compartment

The ML-MFC was fed with AW at the feeding rate of 1.83 ml/min and the current was recorded with different aeration rate to the cathode compartment (Fig. 5). Samples were taken from different point of the reactor for COD determination (Table 1). When the ML-MFC was run without forced aeration the current was around 0.5 mA showing that diffusion cannot supply enough oxygen. The current generation increased as the aeration rate increased up to 100 ml/min.

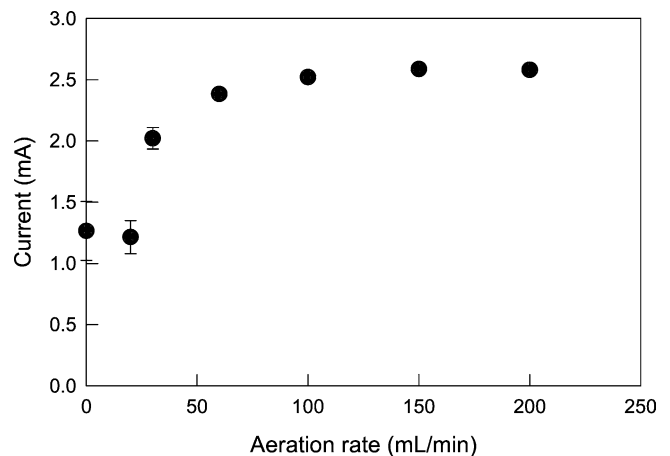


Fig. 5. Effects of aeration rate to the cathode compartment on the current generation.

Table 1
The effects of aeration rate to the cathode on the performance of ML-MFC

Cathode aeration rate (ml/min)	Mean current (mA)	Effluent COD (mg/l)	
		Top part of anode	Cathode compartment
20	1.21 ± 0.15	171.8 ± 7.3	175.2 ± 8.6
30	1.99 ± 0.04	172.3 ± 8.2	161.2 ± 7.4
60	2.37 ± 0.03	177.7 ± 9.1	57.8 ± 5.4
100	2.52 ± 0.03	177.3 ± 9.8	40 ± 5.1
150	2.59 ± 0.05	176.8 ± 9.5	25.3 ± 5.2
200	2.60 ± 0.02	176.0 ± 8.7	14.6 ± 4.3

The COD values in the effluent were much lower than those of samples taken from the top of the anode suggesting that organic compounds were oxidized at the cathode region, probably through the aerobic bacterial respiration (Table 1). Since the critical oxygen concentration of the graphite electrode (6.6 mg/l) is much higher than an aerobic bacterial respiratory system [13], oxygen would be consumed predominantly through aerobic bacterial respiration in the cathode under the condition with the DO concentration lower than the critical oxygen concentration of the electrode restricting the cathode reaction. These results show that an ML-MFC should be operated with the DO concentration higher than the critical oxygen concentration of the cathode, and that this device can be an efficient wastewater treatment process with energy recovery at the anode through the action of electrochemically active anaerobes, and removing the remaining contaminants through aerobic microbes at the cathode.

The current yield was less than 10% throughout the study. This is much lower than that of a MFC with membrane [7]. Based on the result that a major part of the electrons available from the fuel oxidation was not recovered as current, it is hypothesized that electrons are consumed at the anode reducing oxygen diffused from the cathode region. The use of cathode with a critical oxygen concentration comparable to the aerobic bacteria might increase the current yield by reducing oxygen diffusion to the anode and improve the performance of the fuel cell with better cathode reaction.

3.5. Improvement of cathode reaction

The current yield was very low in the above experiments, most probably due to poor cathode reaction. Studies were made to improve the cathode reaction.

3.5.1. Effects of platinum-coated graphite an cathode

The ML-MFC was operated at the fuel-feeding rate of 0.28 ml/min and aeration rate of 60 ml/min, and the current was monitored before and after the graphite cathode (apparent area; 465 cm²) was replaced by platinum-coated graphite (apparent area; 89 cm²). As shown in Fig. 6, higher current (3.2 mA) was generated when the platinum-coated graphite was used than the fresh graphite (2.0 mA), though the apparent area of the former was much smaller than the

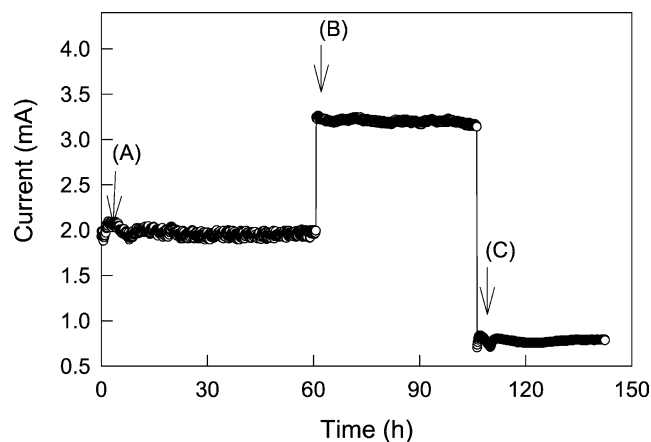


Fig. 6. Current generation by ML-MFC with different cathode. The reactor was run with graphite felt (A, surface area of 465 cm²), platinum-coated graphite felt (B, 89 cm²), and graphite felt (C, 89 cm²) as the cathode.

latter. To compare the effects of platinum-coating, the coated electrode was replaced with the same size fresh graphite (apparent area; 89 cm²). After the cathode replacement the current dropped from 3.2 to 1.0 mA. The current yield of platinum-coated electrode and fresh electrode were about 20 and 13%, respectively. These results show that the performance of ML-MFC can be improved by employing a cathode with higher affinity for oxygen.

3.5.2. NaCl addition to the cathode compartment

While the ML-MFC was operated at the fuel feeding rate of 1.83 ml/min and aeration rate of 200 ml/min, the liquid content of cathode compartment was replaced with 1 M NaCl or continuously fed with 1 M NaCl at the same rate as the fuel feeding rate to monitor the current changes. As shown in Fig. 7, when NaCl was added to the cathode, the current increased from 3.5 up to 4.7 mA, and even higher current of 7.7 mA was generated with the continuous salt feeding.

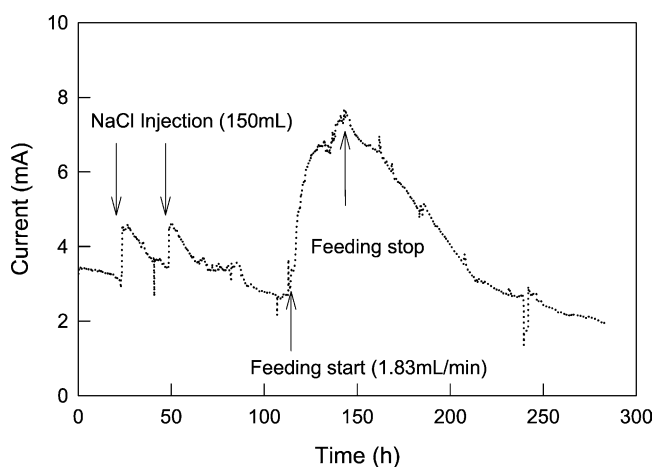


Fig. 7. Current generation with NaCl addition to the cathode as electrolyte. The NaCl solution (1 M) was fed to the bottom of cathode compartment either by injection (150 ml) or continuously (1.83 ml/min) as indicated in the figure by arrow.

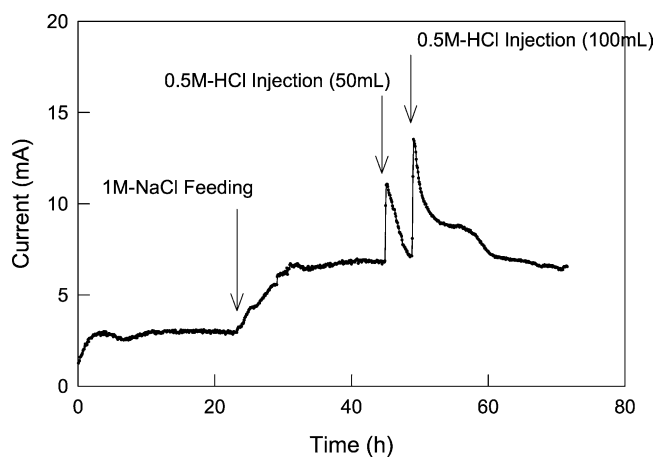


Fig. 8. Cathode acidification and current generation. While the cathode was fed with NaCl continuously, 50 or 100 ml HCl (0.5 N) was injected as indicated in the figure.

NaCl is generally used as electrolyte to improve the mass transfer of charged particles [6]. The increase in the fuel cell performance by NaCl seems due to the increased proton availability to the cathode. This process can be applied to marine environment with better performance as reported by Reimers et al. and Tender et al. [14,15].

3.5.3. Acidification of cathode

In order to confirm that the proton availability is a limiting factor for the cathode reaction, the current was monitored after 0.5 N HCl was injected to the bottom of the cathode to acidify the electrode. As shown in Fig. 8, the current increased to around 7.7 mA with NaCl addition. The current increased further to 11.5 and 13.5 mA after the acidification using 50 and 100 ml HCl solution. The pH at the top of the anode did not fall below 6.5 during the experiment. These results suggest that the proton availability to the cathode is one of the limiting factors of current generation in the ML-MFC.

4. Conclusion

A membrane-less fuel cell-type electrochemical device was developed and used successfully to enrich electrochemically active microbes that converted organic contaminants to electricity. Since the wastewater flow through anaerobic as well as aerobic zone, proper operation of this device can achieve treatment of wastewater containing organic contaminants. The COD removal rate of 526.67 g/m³ day was achieved. The design used in this study showed poor cathode reaction allowing a large quantity of oxygen to diffuse toward the anode. Based on the results studies are being made to improve the design of ML-MFC with higher current yield and better COD removal efficiency.

Acknowledgements

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